(19) JAPANESE PATENT OFFICE (JP)
(12) PATENT JOURNAL (A)
(11) KOKAI PATENT NO. HEI 4[1992]-61703

(43) Publication Date: February 27, 1992
(51) Int. Cl.^{5}: H01B 1/22
C09D 5/24
179/08
H05K 1/09
Sequence Nos. for Office Use: 7244-5G
7211-4J
8830-4J
8727-4E
No. of Inventions: 2 (Total of 8 pages)
Examination Request: Not requested

(54) ELECTRICALLY CONDUCTIVE PASTE FOR PRINTING

(21) Application No.: Hei 2[1990]-169071
(22) Application Date: June 27, 1990

(72) Inventor: Mitsuaki Miyazaki
1-306, 3-13-1 Sakuradai
Isehara, Kanagawa
(72) Inventor: Hiroyoshi Murayama
5-401, 3-1 Takiyama
Higashikurume, Kanagawa
(71) Applicant: Hisoole K.K.
2050 Kamiyabe
Totsukaku, Yokohama
Kanagawa
(74) Agents: Kozo Yuasa, patent attorney, and three others

[There are no amendments to this patent.]

CLAIMS

1. Printable electrically conductive paste characterized by being an electrically conductive paste for circuit and electrode formation, consisting of (A) solvent, (B) thermosetting resin (binder), and (C) electrically conductive metal powder with:

(A) the solvent being at least one chosen from ethylene glycol monophenyl ether, propylene glycol monophenyl ether, ethylene glycol monobenzyl ether, and 2-phenoxyethyl acetate;

(B) the thermosetting resin being one or more polyimide(s) having a solubility of at least 10 wt% in solvent (A) at room temperature;

(C) the electrically conductive metal powder being one or more highly electrically conductive metal powder(s) chosen from gold, silver, palladium, copper, nickel, aluminum, and alloys thereof.

2. The printable electrically conductive paste described in the Claim 1, wherein for solvent (A), at least one solvent chosen from ethylene glycol monophenyl ether, propylene glycol monophenyl ether, ethylene glycol monobenzyl ether, and 2-phenoxyethyl acetate is used together with at least one solvent chosen from diethylene glycol monobutyl ether acetate, 2-butoxyethyl acetate, diethylene glycol dibutyl ether, and ethylene glycol dibutyl ether.

DETAILED EXPLANATION OF THE INVENTION

INDUSTRIAL APPLICATION FIELD

The present invention concerns electrically conductive pastes that can be used for circuits and electrodes that are conductive parts in forming wiring circuits in electric devices, etc.

CONVENTIONAL TECHNOLOGY

Conventionally, e.g., as shown in Japanese Kokai Patent No. Sho 54[1979]-23639, electrically conductive pastes have been used for wiring circuit formation such as printed circuit boards, etc. Such conductive pastes consist of about 60-90 wt% of a conductive metal powder (copper or silver) and about 40-10 wt% of a binder consisting of mainly a thermosetting resin such as an epoxy resin or phenolic resin; such conductive pastes are printed through a screen at a thickness of about 15-35 μ in a desired circuit pattern on a substrate, then heat cured under curing conditions (about 80-220°C) of the binder resin to form a conductor circuit.

The epoxy resins and phenolic resins used as the binder resins have excellent adhesive properties, a large freedom of solvent selection, and handling ease, while the heat resistance is not very good and the reliability at high temperatures is not sufficient. In particular, when the paste is used for electrodes, the solder connection is not very reliable.

Recently, for enhancing the heat resistance of such pastes, e.g., as shown in Japanese Kokai Patent Nos. Sho 54[1979]-126999 and Sho 63[1988]-226811, polyimide resins have been considered for the binder resins. The polyimide resins that can be used as binders include solutions of a polyamic acid that is a polyimide resin precursor in a solvent such as N-methylpyrrolidone (hereafter referred to as NMP) or 2-pyrrolidones and solutions of bismaleimide or modified bismaleimide resin in NMP. Pastes formed by mixing a highly conductive metal powder with the binder solution are transferred onto a substrate via screen printing, then subjected to a polyamic acid ring-closure reaction, thermal polymerization of the bismaleimide resin, or an addition reaction with a polyamine to form a conductive circuit on the substrate.

However, for the conventional resins forming an imide-group-containing molecular structure upon curing or containing imide groups in the molecular structure even before curing, the solvents that can be used are rather limited. Such resins are soluble only in high boiling solvents such as NMP, 2-pyrrolidone, dimethyl sulfoxide, sulfolane, etc., which are highly hygroscopic, polar, and have a high dissolving power. Without such solvents, polyimide resins cannot be made into liquid form. The conductive pastes using polyimide resins as binders contain a small to large amount of such solvents and undergo moisture absorption to evaporation during screen printing, resulting in changes in the paste compositions with respect to viscosity, leading to problems in continuous printing. Serious problems also include the fact that such solvents swell or deteriorate the organic part, such as squeeze rubber of the screen printer and screen emulsion, leading to early wear of the squeeze rubber and screen errors early on, shortening the screen service life.

Thus, in conventional technology, e.g., as shown in Japanese Kokai Patent No. Sho 54[1979]-78491, the polyimide binder resins are modified, concentrating on the development of polyimide resins that can be used with a very small amount of NMP or dimethyl sulfoxide, and can be dissolved or dispersed by adding a solvent commonly used in thick film formation, e.g., diethylene glycol monobutyl ether acetate (hereafter referred to as BCA).

PROBLEMS TO BE SOLVED BY THE INVENTION

As described above, in the printable conductive pastes using polyimide resin binders, a slight improvement in solubility in solvents is made by lowering the resin molecular weight and changes in the molecular structure in the case of polyamic acids and modification by epoxy

resins, etc., in the case of bismaleimide resins. Thus, the high heat resistance characteristic of polyimide resins is sacrificed, and to make conductive pastes using such polyimide resins as binders, the liquid form cannot be obtained without using polar solvents such as NMP. As a result, a fundamental printability improvement cannot be achieved, and compared with thick film pastes using other resins or glass frits as binders, there is a distinct difference in printability with a poor printability due to the viscosity change by moisture absorption, squeeze-rubber early wear, and screen early wear, as well as a poor continuous printability. Thus, they cannot be used widely.

On the other hand, for the polyimide resins, for improving the solubility in solvents, the heat resistance is sacrificed. In particular, as described above, a sufficient reliability cannot be obtained in connections with solders, etc.

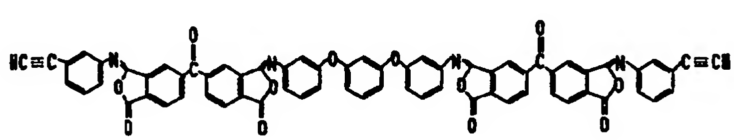
OBJECTIVES OF THE INVENTION

The present invention eliminates problems encountered with the printable conductive pastes using the polyimide resins as the binders as described above. Namely, it is the first objective of the present invention to provide conductive pastes having excellent printability and containing no solvent having a high moisture absorption and strong polarity, such as NMP. It is the second objective of the present invention to provide conductive pastes forming heat-resistant cured products showing sufficient reliability of solder connections, etc.

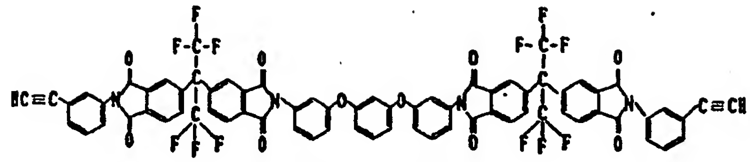
MEANS FOR SOLVING THE PROBLEMS

To achieve such objectives, we started to research polyimide resins that are soluble in solvents with low moisture absorption and no strong polarity, such as BCA, etc. most commonly used in thick film pastes. We have discovered polyimide resins that are very slightly soluble in BCA and can be dissolved in a high concentration in triethylene glycol dimethyl ether (hereafter referred to as triglyme) and tetraethylene glycol dimethyl ether.

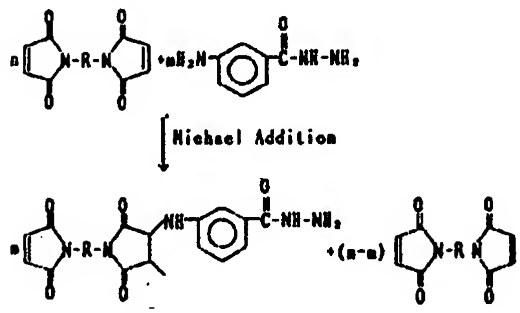
Such polyimide resins are (1) acetylene-terminated polyisoimide oligomers (shown by structures I and II below), (2) copolymer of bismaleimide and amino acid hydrazide (reaction equation I), (3) polyfunctional maleimide resin (structure III), etc.



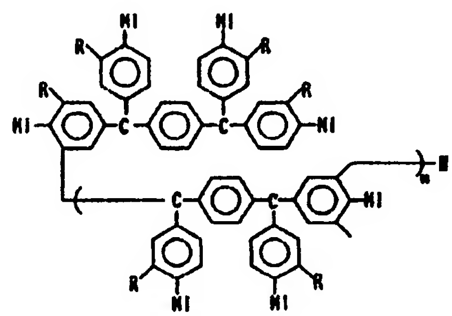
(Structure I)



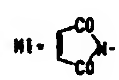
(Structure II)



(Reaction equation I)



(Structure III)



We also discovered that such polyimide resins can be dissolved to a high concentration exceeding 10 wt% at room temperature in high boiling solvents with a limited water content, such as benzene-ring-containing alkylene glycol ethers, e.g., propylene glycol monophenyl ether (hereafter referred to as PGPE), ethylene glycol monobenzyl ether, ethylene glycol monobenzyl ether, 2-phenoxyethyl acetate, etc.

Such polyimide resins are readily available commercially: Thermid IP-600 and FA-7001 (Kanebo NSC) for (1), Compimide #183, #353, and #795 (Boots Company PLC, Technochemie Gmbh) for (2), and MP-2000X, MP-256, and MP-276 (Mitsubishi Yuka) for (3).

The present invention is achieved by dissolving one or more of the polyimide resins described above to a concentration of 10-60 wt% in a benzene-ring-containing alkylene glycol ether such as PGPE, ethylene glycol monobenzyl ether, etc., then mixing with 60-90 wt% of one

or more highly conductive metal powders such as gold, silver, palladium, copper, nickel, aluminum, alloys thereof, etc.

In addition to one or more of the benzene-ring-containing alkylene glyhcol ether solvents described above, one or more high boiling solvent(s) with a limited water content, such as alkylene glycols, e.g., BCA, 2-butoxyethyl acetate, diethylene glycol dibutyl ether, ethylene glycol dibutyl ether, etc., can also be used.

The polyimide resins, solvents, and metal powders can be kneaded together, or various additives may be used for improved viscosity and printability.

ACTION

Compared with conductive pastes using conventional polyimide resins, polymer conductive pastes mainly consisting of one or more of the above polyimide resins, benzene-ring-containing alkylene glycol ether, and highly conductive metal powder are excellent with respect to storage stability and have a markedly improved screen printability.

Using benzene-ring-containing alkylene glycol ether solvents and a selection of polyimide resins soluble in such solvents, with complete elimination of the use of highly polar hygroscopic solvents such as NMP and dimethyl sulfoxide from the paste compositions, problems encountered with conductive pastes using conventional polyimide resins during printing can be entirely eliminated. The benzene-ring-containing alkylene glycol ethers have a slow evaporation rate at room temperature and low moisture absorption, thus there will be no changes in the viscosity of the paste during printing and no adverse effects of solvents such as swelling and wear of the squeeze rubber of the printing machine and screen emulsion, resulting in a markedly extended screen and squeeze rubber service life, leading to an extended continuous printability.

Compared with conductive pastes using other conventional resins, e.g., epoxy resins, phenolic resins, acrylic resins, polyurethane resins, etc., as the binders, the conductive pastes of the present invention have excellent heat resistance and cured film properties.

Some of these excellent properties are:

(1) The sheet resistance is very low at 5-10 mΩ, and a very fine circuit can be made;

(2) Solder wetting is very good with a very high solder strength;

(3) In the thermal aging test after soldering, even after 1000 h at 150°C, the initial strength is completely maintained.

(4) While connections such as wire bonding, etc., have been conventionally impossible for conductive pastes using resin binders, such connections are possible with the conductive pastes of the present invention.

Namely, the conductive pastes of the present invention show improvements not only in screen printability, but also in the cured film properties.

APPLICATION EXAMPLES

Next, the present invention is explained in detail with application examples. Parts are by weight.

APPLICATION EXAMPLE 1

75 parts of flaked silver powder (average particle diameter 8 μ, Fukuda Kinzoku Hakufun Kogyo, AgC-L), 15 parts of polyimide resin Thermid FA-7001, and 22 parts of PGPE solvent were weighed, dissolved, and mixed using a stirrer, kneaded using a 3-roll mill, and treated with small amounts of leveling agent and defoamer, then 3 parts of PGPE, to obtain a paste with a viscosity of about 50-80 Kcps [sic]. This paste was screen printed via a 200-mesh stainless screen on an alumina substrate or polyimide film. This paste did not deteriorate the screen emulsion and squeeze rubber, and had an excellent continuous printability.

After being printed, the printing was dried at 120°C for 10 min, then cured at 360°C for 30 min to obtain a circuit with a film thickness of about 15 μ. The circuit had a sheet resistance 6.1 mΩ/square and soldered-part adhesive strength above 7 kg without wire breakage or substrate failure. The wire bonding strength was about 15-20 g at a wire diameter of 25 μ.

APPLICATION EXAMPLES 2-4

The method of Application Example 1 was repeated with variations of the type of polyimide resin and the amount of PGPE used to obtain pastes which were screen printed. Printing results are shown in Table I and the cured film properties are shown in Tables III-IV.

APPLICATION EXAMPLE 5

70 parts of flaked silver powder (average particle diameter 5 μ, Tokuryoku Kagaku Kenkyusho, TCG-7N), 5 parts of palladium powder (average particle diameter 0.3 μ, Mitsui Kinzoku Kogyo), 15 parts of polyimide resin Thermid FA-7001, and 22 parts of PGPE solvent were weighed, dissolved, and mixed using a stirrer, kneaded using a 3-roll mill, and treated with small amounts of leveling agent and defoamer, then 8 parts of BCA, to obtain a paste with a viscosity of about 50-80 Kcps. Screen printing was carried out similarly as in Application Example 1. Printing results are shown in Table I and the cured film properties are shown in Tables III-IV.

APPLICATION EXAMPLES 6-11

The method of Application Example 5 was repeated with variations of the type of polyimide resin and the amount of BCA used to obtain pastes, which were screen printed. Printing results are shown in Tables I and II and cured film properties are shown in Tables III-IV.

APPLICATION EXAMPLE 12

A paste was prepared similarly as in Application Example 5 from 75 parts of flaked silver powder TCG-7N, 8 parts of polyimide resin Thermid IP-600, 7 parts of MP-256, and 11 parts of BCA solvent, then used for screen printing. Printing results are given in Table II and the cured film properties are given in Tables IIII-IV.

APPLICATION EXAMPLES 13-14

The method of Application Example 12 was repeated with variations of the type of polyimide resin and the amount of BCA used to obtain pastes, which were screen printed. Printing results are shown in Table II and cured film properties are shown in Tables III-IV.

APPLICATION EXAMPLE 15

A paste was prepared similarly as in Application Example 13 from 35 parts of flaked silver powder TCG-7N, 35 parts of AgC-L, 5 parts of palladium powder, 10 parts of polyimide resin Thermid IP-600, and 5 parts of MP-256, then used for screen printing. Printing results are given in Table II and the cured film properties are given in Tables IIII-IV.

APPLICATION EXAMPLE 16-17

The method of Application Example 15 was repeated with variations of the type of polyimide resin to obtain pastes, which were screen printed. Printing results are shown in Table II and cured film properties are shown in Tables III-IV.

APPLICATION EXAMPLE 18

Application Example 12 was repeated using flaked silver powder, polyimide resin, and PGPE and BCA solvents in the same amounts as Application Example 12 with dissolution and mixing using a stirrer and kneading in a 3-roll mill.

The paste viscosity, appearance, etc., were the same as in Application Example 12. Printing results and curing film properties were the same as in Application Example 12.

Table I

Application example	Resin (parts by weight)	Solvent (parts by weight)	Printability (initial)	Printability (continuous)
1	Thermid FA-7001, 15 parts	PGPE, 25 parts	Good	Good
2	Thermid IP-600, 15 parts	PGPE, 26 parts	"	"
3	Compimide #353, 15 parts	PGPE, 23 parts	"	"
4	MP-2000X 15 parts	PGPE, 24 parts	"	"
5	Thermid EA-7001, 15 parts	PGPE, 22 parts BCA, 8 parts	"	"
6	Thermid IP-600, 15 parts	PGPE, 22 parts BCA, 8 parts	"	"
7	Compimide #353 15 parts	PGPE, 22 parts BCA, 6 parts	"	"
8	Compimide #183 15 parts	PGPE, 22 parts BCA, 6 parts	"	"
9	MP-2000X 15 parts	PGPE, 22 parts BCA, 5 parts	"	"

Table II

Application example	Resin (parts by weight)	Solvent (parts by weight)	Printability (initial)	Printability (continuous)
10	MP-256 15 parts	PGPE, 22 parts BCA, 5 parts	Good	Good
11	MP-276 15 parts	PGPE, 22 parts BCA, 5 parts	"	"
12	IP-600, 8 parts MP-256, 7 parts	PGPE, 16 parts BCA, 11 parts	"	"
13	IP-600, 10 parts MP-2000X, 5 parts	PGPE, 16 parts BCA, 12 parts	"	"
14	IP-600, 10 parts #353, 5 parts	" "	"	"
15	IP-600, 10 parts MP-256, 5 parts	" "	"	"
16	IP-600, 10 parts MP-2000X, 5 parts	" "	"	"
17	IP-600, 10 parts #353, 5 parts	" "	"	"
18	IP-600, 8 parts MP-256, 7 parts	PGPE, 16 parts BCA, 11 parts	"	"

Table III

	Storage stability (+20°C)	Curing conditions (°C/min)	Sheet resistance (mΩ/□)
Application Example 1	More than 3 months	360/30	6.1
" 2	"	"	5.8
" 3	"	320/30	5.5
" 4	"	340-30	5.8
" 5	"	360/30	16.8
" 6	"	"	15.2
" 7	"	320/30	12.8
" 8	"	"	13.5
" 9	"	340/30	11.4
" 10	"	280/30	14.6
" 11	"	"	14.2
" 12	"	350/30	5.7
" 13	"	360/30	6.8
" 14	"	"	4.7
" 15	"	"	12.8
" 16	"	"	13.5
" 17	"	"	10.1
" 18	"	350/30	5.7

Table IV

	Solder wetting	Solder strength (kg/2 mm pad)		Bonding strength (g)
		Alumina	Polyimide	
Application Example 1	Good	More than 7 kg	More than 7 kg	15-20
" 2	"	"	"	"
" 3	"	"	6-7 kg	10-15
" 4	"	"	5-6 kg	"
" 5	"	"	More than 7 kg	15-20
" 6	"	"	"	"
" 7	"	"	6-7 kg	10-15
" 8	"	"	"	"
" 9	"	"	5-6 kg	"
" 10	"	"	"	"
" 11	"	"	"	"
" 12	"	"	More than 7 kg	15-20
" 13	"	"	"	"
" 14	"	"	"	"

" 15	"	"	"	10-15
" 16	"	"	"	"
" 17	"	"	"	"
" 18	"	"	"	15-20

COMPARATIVE EXAMPLE 1

A paste was prepared from 75 parts of flaked silver powder TCG-7N, 15 parts of polyimide resin Kerimid #601 (Nippon Polyimide Co.), and 50 parts of NMP solvent by dissolving and mixing in a stirrer, then kneading in a 3-roll mill. The as-prepared paste had a viscosity of about 40 Kcps and gelled in about 7 days at room temperature.

The as-prepared paste showed a very poor printability; due to early deterioration of the squeeze rubber, continuous printing was not possible.

After being cured at 260°C for 30 min, the sheet resistance could not be measured, due to shorting caused by line sagging. The cured film was not wettable by solder.

COMPARATIVE EXAMPLE 2

A paste was prepared similarly as in Comparative Example 1 using 90 parts of the polyimide resin PSI-ZPS-1514 (Chisso, resin content 17%, solvent composition NMP/BCA = 70/50). The as-prepared paste had a viscosity of about 40 Kcps and exhibited silver powder sedimentation in 2-3 days at room temperature.

Similar to Comparative Example 1, the as-prepared paste exhibited a very poor screen printability, and continuous printing was not possible.

After being cured at 260°C for 30 min, the sheet resistance could not be measured similarly as in Comparative Example 1, and solder wettability was not observed.

COMPARATIVE EXAMPLE 3

A paste was prepared similarly as in Comparative Example 1 using 54 parts of the polyimide resin LARC-TPI (Mitsui Toatsu Kagaku, 28% triglyme solution). The as-prepared paste showed a viscosity of about 50 Kcps. Sedimentation of the powder was observed similarly as in Comparative Example 2. While the screen printability of the as-prepared paste was very poor, there was no deterioration of the squeeze rubber, etc.

The film properties after being cured at 260°C for 30 min were comparable to those of Comparative Example 2.

COMPARATIVE EXAMPLE 4

A paste was prepared similarly as in Comparative Example 1 using 25 parts of the polyimide resin SR-5110 (Nissan Kagaku Kogyo, resin concentration 60 wt%, in NMP/BCA mixed solvent) and 8 parts of BCA added for viscosity control. The as-prepared paste had a viscosity of about 60 Kcps. The paste could be used even after being stored for about 20 days at room temperature.

Table V

Comparative example	Resin (parts by weight)	Solvent (parts by weight)	Printability (initial)	Printability (continuous)
1	Kerimid #601 15 parts	NMP, 45 parts	Good	Impossible
2	PSI-ZPS-1514 90 parts	NMP, 44 parts BCA, 31 parts	"	"
3	LARC-TPI 54 parts	Triglyme, 39 parts	"	Good
4	SR-5110 25 parts	NMP+BCA =10 parts	Poor	"

Table VI

	Storage stability (+20°C)	Curing conditions (°C/min)	Sheet resistance (mΩ/□)
Comparative Example 1	About 1 week	260-30	12.5
" 2	> 3 months	"	21.5
" 3	"	"	24.0
" 4	About 20 days	240/30	9.2

Table VII

	Solder wetting	Solder strength (kg/2 mm pad)		Bonding strength (g)
		Alumina	Polyimide	
Comparative Example 1	Poor	More than 7 kg	More than 7 kg	15-20
" 2	"	-	-	-
" 3	"	-	-	-
" 4	Good	6-7 kg	5-6 kg	-

While the as-prepared paste had a good screen printability, the continuous printability was poor, due to deterioration of the squeeze rubber, etc.

The film properties after being cured are given in Tables VI-VII.

EFFECTS OF THE INVENTION

As explained with the examples above, in the conductive pastes using polyimide resin binders, and using certain solvent components and highly heat-resistant thermosetting polyimide resin components with a small imide group equivalent, it is possible to obtain an improved paste storage stability, very good printability, and continuous thick printing.

Furthermore, cured film properties comparable or superior to the thick film pastes using glass frit binders can be realized.

Compared with conductive pastes using conventional glass frit binders with substrates limited to ceramics, the conductive pastes of the present invention can be used for heat-resistant organic substrates of polyimide resins and for glass substrates and ceramic substrates.

Applicant: Hakuto Kagaku K.K. (this is not on the front page)
Agents: Kozo Yuasa, patent attorney, and three others.

Language Services Unit
Phoenix Translations
February 7, 2002